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Nonequilibrium Ornstein-Zernike relation for Brownian many-body dynamics

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We derive a dynamic Ornstein-Zernike equation for classical fluids undergoing overdamped Brownian motion and driven out of equilibrium. Inhomogeneous two-time correlation functions are obtained from functional differentiation of the one-body density and current with respect to an appropriately chosen external field. Functional calculus leads naturally to non-Markovian equations of motion for the two-time correlators. Memory functions are identified as functional derivatives of a space- and time-nonlocal power dissipation functional. We propose an excess (over ideal gas) dissipation functional that both generates mode-coupling theory for the two-body correlations and extends dynamical density functional theory for the one-body fields, thus unifying the two approaches.

I. INTRODUCTION

In 1914 Leonard Ornstein and Frits Zernike developed a theory of critical opalescence in which they proposed to separate the radial distribution function, $g(r)$, into direct and indirect contributions.[1] The Ornstein-Zernike (OZ) relation, which has since become a cornerstone of equilibrium liquid-state theory,[2] provides the mathematical expression of this separation and defines the direct correlation function, $c(r)$, via the integral relation

$$h(r_{13}) = c(r_{13}) + \rho_b \int d\mathbf{r}_2 \; c(r_{12}) h(r_{23}), \qquad (1)$$

where ρ_b is the bulk number density, $h(r) = g(r) - 1$ is the total correlation function, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The strength of this approach lies in the fact that $c(r)$ usually has a simple functional dependence on both the separation r and on ρ_b, thus facilitating the development of approximations. By supplementing the OZ relation with an appropriate closure relation between $h(r)$ and $c(r)$, one arrives at a closed integral equation theory for the equilibrium pair correlations, and hence for all thermodynamic properties of the system.[2] Even simple, short-ranged approximations to $c(r)$ can describe accurately the oscillatory behaviour of $g(r)$, which arises from molecular packing effects, and can capture the long-ranged decay of $g(r)$ near the critical point,[3] which causes the experimentally observed turbidity.

Deeper insight into the OZ equation (1), as well as its natural extension to inhomogeneous systems, is provided by modern density functional theory (DFT).[4] Within DFT the direct correlation function, $c(\mathbf{r}_1, \mathbf{r}_2)$, is defined as the second functional derivative of the excess (over ideal gas) Helmholtz free energy with respect to the density. A second generating functional, the grand potential, is obtained from Legendre transform of the Helmholtz free energy and yields the density-density correlation function, $\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2) + \rho(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2)$, upon differentiation with respect to the external potential; here $\rho(\mathbf{r})$ is the inhomogeneous one-body density distribution. The inhomogeneous OZ relation,

$$h(\mathbf{r}_1, \mathbf{r}_3) = c(\mathbf{r}_1, \mathbf{r}_3) + \int d\mathbf{r}_2 \; c(\mathbf{r}_1, \mathbf{r}_2)\rho(\mathbf{r}_2)h(\mathbf{r}_2, \mathbf{r}_3), \qquad (2)$$

which reduces to (1) in the absence of an external potential, then expresses the fact that the direct and density-density correlation functions are (essentially) functional inverses of each other. The OZ relation (2) thus plays the role of a fundamental sum rule, distinct from hierarchies that relate, e.g., two-body functions to integrals over three-body functions.[2] Higher-order correlation functions can be obtained by further differentiation of the generating functionals[4] and are interrelated by higher-order OZ relations.[5]

The situation in nonequilibrium is quite different. No analogue of the OZ relation is known that would determine *dynamic* correlation functions.[6] Such a nonequilibrium Ornstein-Zernike (NOZ) equation should fulfill at least three requirements: (i) It should determine the van Hove function, $G_{\mathrm{vH}}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$, which is the natural generalization of $g(\mathbf{r}_1, \mathbf{r}_2)$ to time-dependent situations. (ii) It should be an equation on the two-body level, distinct from the familiar n-body correlation hierarchies.[2] (iii) Direct time correlation functions, which depend on two points in spacetime, should occur, in analogy to $c(\mathbf{r}_1, \mathbf{r}_2)$ in the static case. These conditions are not met by simply adding a time argument to the functions appearing in (2), as has been suggested in the literature.[7]

In this paper we propose a dynamical equation that satisfies all of the above requirements. The derivation is based on the dynamical generalization of the well-known equilibrium concept of functional differentiation as a means to generate n-point correlation functions. We first apply this method to dynamical density functional theory (DDFT),[8] and then supplement the resulting approximate equation by a

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formally exact contribution that involves direct time correlation functions. Furthermore, we show that within the recently introduced power functional framework,[9] the direct time correlation functions can be identified as second functional derivatives of the excess (over ideal gas) power dissipation functional. The NOZ equation may thus be closed via approximation of the excess power dissipation functional, in the spirit of equilibrium DFT. Alternatively, in the spirit of integral equation theory,[2] one can postulate an additional relation between the van Hove and the direct time correlation functions. We show that mode-coupling theory (MCT) can be viewed as providing a closure of the latter type, where the memory function plays the role of a direct time correlation function.

II. THEORY

A. Microscopic dynamics

We describe the state of the system by a time-dependent distribution function $\Psi(\mathbf{r}^N, t)$, which gives the probability density to find the N particles in the system at positions $\mathbf{r}^N \equiv \{\mathbf{r}_1, \ldots \mathbf{r}_N\}$ at time t. The particles interact via an interparticle potential $U(\mathbf{r}^N)$ and with their surrounding via an external potential $V_{\text{ext}}(\mathbf{r}, t)$ and via a non-conservative force field $\mathbf{X}(\mathbf{r}, t)$. The thermal agitation at constant temperature T is balanced by a velocity-dependent friction force with force constant γ. The resulting overdamped Brownian dynamics can be described via the continuity equation for the many-body distribution function,

$$\frac{\partial}{\partial t}\Psi(\mathbf{r}^N, t) = -\sum_i \nabla_i \cdot \hat{\mathbf{v}}_i(t)\Psi(\mathbf{r}^N, t). \tag{3}$$

Here the velocity operator of particle i is defined as

$$\hat{\mathbf{v}}_i(t) = \gamma^{-1}[-(\nabla_i U(\mathbf{r}^N)) - k_{\text{B}}T\nabla_i - (\nabla_i V_{\text{ext}}(\mathbf{r}_i, t)) + \mathbf{X}(\mathbf{r}_i, t)], \tag{4}$$

where k_{B} is the Boltzmann constant, and T is absolute temperature. Within this Smoluchowski picture the average of an operator $\hat{a}(t)$ in configuration space is given by $a(t) = \langle \hat{a}(t) \rangle = \int d\mathbf{r}^N \hat{a}(t)\Psi(\mathbf{r}^N, t)$.

B. One-body averages

For the present study the one-body density and one-body current are of particular importance and are described by the operators

$$\hat{\rho}(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{5}$$

$$\hat{\mathbf{J}}(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\hat{\mathbf{v}}_i(t). \tag{6}$$

For brevity we will henceforth use the shorthand notation $\hat{\rho}(1) \equiv \hat{\rho}(\mathbf{r}_1, t_1)$, and $\hat{\mathbf{J}}(1) \equiv \hat{\mathbf{J}}(\mathbf{r}_1, t_1)$ for spacetime points. The one-body density and current are then given by $\rho(1) = \langle \hat{\rho}(1) \rangle$ and $\mathbf{J}(1) = \langle \hat{\mathbf{J}}(1) \rangle$, respectively. The one-body velocity is simply $\mathbf{v}(1) = \mathbf{J}(1)/\rho(1)$. The local conservation of particle number is expressed by the one-body continuity equation

$$\frac{\partial}{\partial t_1}\rho(1) = -\nabla_1 \cdot \mathbf{J}(1). \tag{7}$$

C. Two-body correlation functions

On the two-body level, the molecular motion of a liquid is commonly analyzed in terms of a two-time density-density correlation function first introduced by Leon van Hove.[2] For spatially and temporally inhomogeneous situations the van Hove function is defined by

$$G_{\text{vH}}(1, 2) = \rho(1)^{-1}\langle \hat{\rho}(1)\hat{\rho}(2) \rangle, \tag{8}$$

where the two-time average is taken with respect to the nonequilibrium distribution at the earlier time t_2, together with the conditional probability for finding the state at the later time t_1.

While the equilibrium relaxation dynamics of the system is well-characterized by the van Hove function, the motion in the presence of, e.g., a time-dependent external potential or non-conservative shear forces is better described by the nonequilibrium two-body function

$$\mathbf{J}^{\text{f}}_{\text{vH}}(1, 2) = \langle \hat{\mathbf{J}}(1)\hat{\rho}(2) \rangle, \tag{9}$$

which we will henceforth refer to as the (front) van Hove current. We adopt the convention $t_1 \geq t_2$. The analogue of (7) on the two-body level is given by

$$\frac{\partial}{\partial t_1}\rho(1)G_{\text{vH}}(1, 2) = -\nabla_1 \cdot \mathbf{J}^{\text{f}}_{\text{vH}}(1, 2), \tag{10}$$

which relates the vectorial van Hove current to the scalar van Hove function.

D. Static functional derivatives

In order to connect the one-time level of description, provided by the density, $\rho(1)$, and current, $\mathbf{J}(1)$, to the inhomogeneous two-time van Hove current, we seek to express the latter as a functional derivative of the former with respect to an appropriately chosen one-body field. In equilibrium this procedure is straightforward. For example, the equilibrium density is given by

$$\rho(\mathbf{r}) = \text{Tr}_{\text{cl}}\hat{\rho}(\mathbf{r})\Psi_{\text{eq}}(\mathbf{r}^N), \tag{11}$$

where Tr_{cl} is the classical trace over phase space and total particle number, and the grand canonical probability density is given by

$$\Psi_{\text{eq}}(\mathbf{r}^N) = \Xi^{-1}e^{-\beta(H-\mu N)}, \tag{12}$$

where Ξ is the grand partition function, $\beta = (k_{\text{B}}T)^{-1}$, $H = \sum_i [\mathbf{p}_i^2/(2m) + V_{\text{ext}}(\mathbf{r}_i)] + U(\mathbf{r}^N)$ is the Hamiltonian, $\mathbf{p}_i$ is the momentum of particle i, m is the particle mass, and μ is the chemical potential.[2] Functional differentiation of the density with respect to its conjugate field, the external potential, generates the density-density correlation function

$$\left.\frac{\delta\rho(\mathbf{r})}{\delta\beta V_{\text{ext}}(\mathbf{r}')}\right|_{\text{eq}} = \langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle - \rho(\mathbf{r})\rho(\mathbf{r}'). \tag{13}$$

Here we use that for fields $u(\mathbf{r})$ that depend only on space $\delta u(\mathbf{r})/\delta u(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$.

E. Dynamic functional derivatives

Out of equilibrium there is no standard procedure for generating, in the spirit of (13), inhomogeneous two-time correlation functions. We thus seek to express microscopic two-time correlators as functional derivatives of one-body fields. Consider the Smoluchowski equation (3) in the form

$$\frac{\partial}{\partial t}\Psi(\mathbf{r}^N,t) = \hat{\Omega}(t)\Psi(\mathbf{r}^N,t), \tag{14}$$

where the (Smoluchowski) time evolution operator, given by

$$\hat{\Omega}(t) = -\sum_i \nabla_i \cdot \hat{\mathbf{v}}_i(t), \tag{15}$$

allows to write the formal solution of (14) as

$$\Psi(\mathbf{r}^N,t) = \mathrm{e}_+^{\int_{t_0}^t ds\,\hat{\Omega}(s)}\Psi(\mathbf{r}^N,t_0), \tag{16}$$

where t_0 is an initial time and e_+ indicates a time-ordered exponential (see, e.g., Ref. 10), which is defined via the power series

$$\begin{aligned}\mathrm{e}_+^{\int_{t_0}^t ds\hat{\Omega}(s)} &= 1 + \int_{t_0}^t ds\hat{\Omega}(s) + \int_{t_0}^t ds_1\int_{t_0}^{s_1} ds_2\hat{\Omega}(s_1)\hat{\Omega}(s_2)\\ &+ \int_{t_0}^t ds_1\int_{t_0}^{s_1} ds_2\int_{t_0}^{s_2} ds_3\hat{\Omega}(s_1)\hat{\Omega}(s_2)\hat{\Omega}(s_3) + \cdots .\end{aligned} \tag{17}$$

The time-ordered exponential in (16) acts as a propagator and will play a role analogous to that of the Boltzmann factor in the equilibrium distribution (12).

In order to calculate the desired functional derivatives we will use the general functional identity $\delta u(\mathbf{r},t)/\delta u(\mathbf{r}',t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$, where $u(\mathbf{r},t)$ is an arbitrary function, and furthermore the chain rule for time-ordered exponentials,

$$\frac{\delta}{\delta u(\mathbf{r},t)}\mathrm{e}_+^{\int_{t_1}^{t_2} ds\,\hat{\Omega}(s)} = \int_{t_1}^{t_2} ds\,\mathrm{e}_+^{\int_s^{t_2} ds'\,\hat{\Omega}(s')}\frac{\delta\hat{\Omega}(s)}{\delta u(\mathbf{r},t)}\mathrm{e}_+^{\int_{t_1}^{s} ds'\hat{\Omega}(s')}. \tag{18}$$

Observing the general definition of the two-time correlation between two operators $\hat{a}(1)$ and $\hat{b}(2)$,

$$\langle\hat{a}(1)\hat{b}(2)\rangle = \int d\mathbf{r}^N\hat{a}(1)\mathrm{e}_+^{\int_{t_2}^{t_1} ds\hat{\Omega}(s)}\hat{b}(2)\mathrm{e}_+^{\int_{t_0}^{t_2} ds\hat{\Omega}(s)}\psi(\mathbf{r}^N,t_0), \tag{19}$$

and using (18) it is straightforward to show that the following functional derivative relations hold

$$\frac{\delta\mathbf{J}(1)}{\delta\beta\mathcal{V}(2)} = I(1,2) + \frac{\partial}{\partial t_2}\mathbf{J}^{\mathrm{f}}_{\mathrm{vH}}(1,2), \tag{20}$$

$$\frac{\delta\rho(1)}{\delta\beta\mathcal{V}(2)} = \rho(1)\frac{\partial}{\partial t_2}G_{\mathrm{vH}}(1,2), \tag{21}$$

where causality requires $t_2 \le t_1$. The functional derivatives are built with respect to the function

$$\mathcal{V}(2) \equiv \int_{t_0}^{t_2} dt_2'\,D_0\nabla_2^2\,V_{\mathrm{ext}}(2'), \tag{22}$$

where we employ the notation $V_{\mathrm{ext}}(2') = V_{\mathrm{ext}}(\mathbf{r}_2,t_2')$. The function $\mathcal{V}(2)$ has the same physical dimension as the external potential, but rather measures the accumulated change in potential arising from the action of the diffusion operator. The instantaneous contribution to (20) is given by $I(1,2) = -\gamma^{-1}\rho(1)\delta\nabla V_{\mathrm{ext}}(1)/\delta\beta\mathcal{V}(2)$; explicit evaluation of the functional derivative in will not be required for the following development.

The consistency of our formalism with the equilibrium density functional approach can be demonstrated by assuming the system was in equilibrium for all times and integrating the dynamic functional derivative (21) over the entire history

$$\int_{-\infty}^{t_2} dt_2'\,\frac{\delta\rho(1)}{\delta\beta\mathcal{V}(2')} = \int_{-\infty}^{t_2} dt_2'\,\rho(1)\frac{\partial}{\partial t_2'}G_{\mathrm{vH}}(1,2') \tag{23}$$

$$= \langle\hat{\rho}(\mathbf{r}_1)\hat{\rho}(\mathbf{r}_2)\rangle - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \tag{24}$$

$$= \frac{\delta\rho(\mathbf{r}_1)}{\delta\beta\,V_{\mathrm{ext}}(\mathbf{r}_2)}\Big|_{\mathrm{eq}}, \tag{25}$$

where we make the (reasonable) assumption that density fluctuations become decorrelated at sufficiently long times. Note that in this dynamical calculation the second term in (24) arises from the lower integration limit, whereas in the standard Gibbs ensemble calculation (13) it is generated by the normalization of the probability distribution.

F. DDFT approximation

We next seek to apply the mathematical framework developed above to generate equations of motion for the two-time correlation functions. This requires explicit expressions for the one-body averages which can be differentiated with respect to the external fields. The simplest theory for the microscopic one-body current of interacting particles is the DDFT,[8] where the current,

$$\mathbf{J}_{\mathrm{DDFT}}(1) = \frac{\rho(1)}{\gamma}\left(-\nabla\frac{\delta F[\rho]}{\delta\rho(1)} - \nabla V_{\mathrm{ext}}(1) + \mathbf{X}(1)\right), \tag{26}$$

expresses a time-local balance between the viscous friction, $\gamma\mathbf{v}(1)$, external forces, forces due to thermal motion, and interparticle interactions, the latter two contributions generated by the intrinsic Helmholtz free energy functional $F[\rho]$. When combined with the one-body continuity equation (7), a closed drift-diffusion equation for $\rho(1)$ follows.

Using (26) to calculate the functional derivative $\delta\mathbf{J}(1)/\delta\beta\mathcal{V}(3)$, employing the functional chain rule, and the relations (20) and (21) generates a DDFT approximation to the van Hove current,

$$\begin{aligned}&\mathbf{J}^{\mathrm{f,DDFT}}_{\mathrm{vH}}(1,3)\\ &= \mathbf{J}(1)G_{\mathrm{vH}}(1,3) - D_0\rho(1)\nabla_1\left(G_{\mathrm{vH}}(1,3)\right.\\ &\left. - \int d\mathbf{r}_2 c(1,2_1)\rho(2_1)\left(G_{\mathrm{vH}}(2_1,3) - \rho(3_{-\infty})\right)\right),\end{aligned} \tag{27}$$

where $\rho(3_{-\infty}) \equiv \rho(\mathbf{r}_3,-\infty)$ and a contribution $\nabla_1\rho(3_{-\infty})$ vanishes. The argument 2_1 in (27) indicates position $\mathbf{r}_2$

and time t_1; the direct correlation function is hence evaluated at distinct values of the spatial arguments at the same time, $c(1, 2_1) \equiv c(\mathbf{r}_1, \mathbf{r}_2, t_1)$, and $\mathbf{v}(1)$ is given here by $\mathbf{J}_{\rm DDFT}(1)/\rho(1)$. Here the equilibrium direct correlation function is the second functional derivative of the excess (over ideal gas) part of the intrinsic Helmholtz free energy, $c(\mathbf{r}_1, \mathbf{r}_2) = -\delta^2\beta F^{\rm exc}[\,\rho]/\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)$.[4] In obtaining (27) we have made the assumption that two-body correlations factorize for widely separated time arguments, i.e., $\langle\hat{\rho}(\mathbf{r}, t)\hat{\rho}(\mathbf{r}', -\infty)\rangle = \rho(\mathbf{r}, t)\rho(\mathbf{r}', -\infty)$, which holds in the absence of an ideal glass transition. The three distinct contributions to (27) represent a transport term, ideal decay, and an adiabatic integral term due to interparticle interactions.

Equation (27) is the natural extension of the DDFT approximation for the one-body current (26) to the two-body level. Substitution of (27) into the two-body continuity equation (10) yields a closed equation for the van Hove function which is local in time, due to the adiabatic assumption underlying (26), but nonlocal in space; this is the DDFT approximation to the NOZ equation we seek. External forces do not appear in (27) explicitly, but enter implicitly via the one-body density and current obtained by solving (7) with (26). The fact that Eq. (27) is closed is a direct consequence of the adiabatic assumption that thermodynamic driving forces can be generated from an equilibrium free energy functional. As we will discuss below, this is equivalent to neglecting the contribution of interparticle interactions to the the power dissipation in the dynamical generating (power) functional.

Within the same DDFT approximation considered here Archer *et al.*[12,13] have proposed a dynamic test-particle method for calculating the equilibrium van Hove function. This alternative approach focuses on the simultaneous relaxation of both a tagged particle density (from a delta-function initial state) and the one-body density distribution of the remaining particles (from initial state $\rho(r, 0) = \rho_b g(r)$). In general, this one-body route to the van Hove function will produce results which differ from those generated by Eqs. (10) and (27). In the special case that the Helmholtz free energy is approximated by a quadratic density expansion (the Ramakrishnan-Yussouff (RY) approximation[14]) the test-particle current becomes identical to (27). The RY functional thus exhibits test-particle self consistency within the DDFT approximation.

G. Equal-time equilibrium correlations

In the special case of equilibrium at all times, $\mathbf{J}(1) = 0$, the equal-time limit, $t_1 = t_3$, of (27) yields

$$\mathbf{J}^{\rm f,DDFT}_{\rm vH}(1, 3_1) = -D_0\rho(1)\nabla_1\Big[\delta(\mathbf{r}_1 - \mathbf{r}_3) + \rho(3_1)\Big(h(1, 3_1) - c(1, 3_1) - \int d\mathbf{r}_2 c(1, 2_1)\rho(2_1)h(2_1, 3_1)\Big)\Big], \tag{28}$$

where we have used the equal time limit of the van Hove function, $G_{\rm vH}(1, 3_1) = \rho(3_1)(h(1, 3_1) + 1) + \rho(1)\delta(\mathbf{r}_1 - \mathbf{r}_3)$. The short-time relaxation of the van Hove function is determined by the highly localised, delta-function initial condition of the self part, such that the term in square brackets in (28) is identically zero. The dynamic functional derivative approach to two-time correlation functions thus provides an alternative derivation of the inhomogeneous OZ equation (2).

H. Homogeneous system without external forces

In the homogeneous limit with no external forces Eq. (27) reduces to

$$\frac{\partial}{\partial t}F(k, t) + \Gamma(k)F(k, t) = 0, \tag{29}$$

where the intermediate scattering function, $F(k, t)$, is the three-dimensional spatial Fourier transform of the translationally invariant equilibrium van Hove function.[2] The time-independent "initial decay rate" is given by $\Gamma(k) = D_0\, k^2/S(k)$, where $S(k) = 1/(1 - \rho_b\tilde{c}(k))$ is the static structure factor; here the tilde indicates the spatial Fourier transform. Equation (29) has the solution

$$F(k, t) = e^{-\Gamma(k)t}. \tag{30}$$

The effective diffusion constant, $D_0/S(k)$, is strongly reduced for wavenumbers around the main peak of $S(k)$, relative to the bare diffusion constant. This well-known "de Gennes narrowing"[11] has its origins in the strong spatial correlations at wavelengths corresponding to the local nearest-neighbour cage around any given particle.

I. Homogeneous system under shear

When applied to a spatially homogeneous systems under steady shear of rate $\dot{\gamma}_s$, with flow in x-direction and shear-gradient in y-direction, Eq. (26) yields $\gamma\mathbf{J}_{\rm DDFT}(1)/\rho_b = \mathbf{X}(1) \equiv \dot{\gamma}_s y_1\hat{\mathbf{e}}_x$. Solution of Eqs. (10) and (27) for this one-body current is straightforward (using, e.g., the method of characteristics) and yields

$$F(\mathbf{k}, t) = \exp\left(-\frac{\mathbf{kk}:\mathbf{D}(t\,;\dot{\gamma}_s)}{S(k(t))}\right), \tag{31}$$

in which the wavevector dyadic $\mathbf{kk}$ is fully contracted with the time-dependent diffusion tensor, given by

$$\mathbf{D}(t\,;\dot{\gamma}_s) = \begin{pmatrix} t + \frac{\dot{\gamma}_s^2 t^3}{3} & \dot{\gamma}_s t^2 & 0 \\ 0 & t & 0 \\ 0 & 0 & t \end{pmatrix}, \tag{32}$$

and where the shear-advected wavevector is given by $\mathbf{k}(t) = (k_x, k_y + \dot{\gamma}_s k_x t, k_z)$. Equation (31) extends (30) to steadily sheared states and captures the enhanced diffusion in flow direction, termed "Taylor dispersion,"[15] which arises from the coupling of Brownian and affine motion. Equation (27) thus treats systems with non-zero density by supplementing the exact low density limit (Eq. (31) with $S(k) = 1$) with an approximate, wavevector dependent diffusion tensor. The approximation (31) is on a similar level to the fluctuating diffusion equation approach of Ronis[16] (for a review of alternative approaches to calculating the distorted structure factor see Ref. 17).

J. Beyond DDFT

In contrast to the DDFT approximation (27), the exact expression for $\mathbf{J}^{\mathrm{f}}_{\mathrm{vH}}(1,2)$ should include the physics of structural relaxation, via a dependence on the history of both one- and two-body correlation functions. Introduction of vectorial and tensorial direct time correlation functions, denoted by $\mathbf{m}(1,2)$ and $\mathsf{M}(1,2)$, respectively, enables formulation of a general equation of motion. Splitting the full van Hove current into the DDFT contribution and an irreducible part, $\mathbf{J}^{\mathrm{f}}_{\mathrm{vH}} = \mathbf{J}^{\mathrm{f,DDFT}}_{\mathrm{vH}} + \mathbf{J}^{\mathrm{irr}}_{\mathrm{vH}}$, we identify the most general non-Markovian form that involves only one- and two-body functions which generate a vector field from spacetime convolutions of the van Hove function and van Hove current, namely,

$$\begin{aligned}\mathbf{J}^{\mathrm{irr}}_{\mathrm{vH}}(1,3) = \mathbf{J}^{\mathrm{irr}}_{\mathrm{vH}}(1,3_{-\infty}) - \rho(1)\int_{-\infty}^{t_3} dt_3'\,\nabla_3\cdot\mathsf{M}(1,3')\rho(3') \\ + \rho(1)\int d2\,\big[\mathsf{M}(1,2)\cdot\big(\mathbf{J}^{\mathrm{f}}_{\mathrm{vH}}(2,3) - \mathbf{J}(2)\rho(3_{-\infty})\big) \\ + \mathbf{m}(1,2)\rho(2)(G_{\mathrm{vH}}(2,3) - \rho(3_{-\infty}))\big].\end{aligned} \tag{33}$$

The 2-integral in (33) runs over a spacetime slab from the earlier time t_3 to later time t_1, consistent with causality. Unlike the approximate DDFT expression (27), the exact NOZ equation is not closed and serves to define the direct time correlation functions $\mathbf{m}(1,2)$ and $\mathsf{M}(1,2)$, in analogy to the equilibrium OZ equation (2), which defines the static direct correlation function $c(\mathbf{r}_1,\mathbf{r}_2)$. Equation (33), when combined with (27), provides a natural generalization of the equilibrium OZ equation to nonequilibrium systems undergoing Brownian dynamics and enables structural relaxation to be incorporated via the time direct correlation functions. Although the continuity equation (10) can be used to eliminate $\mathbf{J}^{\mathrm{f}}_{\mathrm{vH}}(1,3)$ from (33) in favour of $G_{\mathrm{vH}}(1,3)$, closure still requires that (33) be supplemented by two independent equations that relate $\mathbf{m}(1,2)$ and $\mathsf{M}(1,2)$ to the van Hove function and its current. This can be achieved either by postulating closure relations (as is done in equilibrium via, e.g., the Percus-Yevick or hyper-netted-chain approximations,[2]) or by exploiting the power functional formalism,[8] as outlined below.

An approximation of particular significance is obtained by setting $\mathbf{m}(1,2) = 0$, neglecting the second direct (without spatial convolution) term, and simplifying the tensorial structure of the remaining direct time correlation function, $\mathsf{M}(1,2) = M(1,2)\mathbf{1}$, where $M(1,2)$ is a scalar function and $\mathbf{1}$ the unit matrix. For homogeneous equilibrium states the general equation (33) then reduces to

$$\frac{\partial}{\partial t}F(k,t) + \Gamma(k)F(k,t) - \int_0^t dt'\,\tilde{M}(k,t-t')\dot{F}(k,t') = 0, \tag{34}$$

which is a non-Markovian equation for the intermediate scattering function, identical to that employed in MCT. The standard "idealized" mode-coupling theory[18] is obtained by setting $\tilde{M}(k,t) = \tilde{M}_{\mathrm{MCT}}(k,t)$, where the friction kernel given by

$$\tilde{M}_{\mathrm{MCT}}(k,t) = -\frac{\rho_b\Gamma(k)}{16\pi^3}\int d\mathbf{q}\;V(\mathbf{k},\mathbf{q})\,F(q,t)F(|\mathbf{k}-\mathbf{q}|,t), \tag{35}$$

contains the vertex function

$$V(\mathbf{k},\mathbf{q}) = \frac{S(k)S(q)S(p)}{k^4}(\mathbf{k}\cdot\mathbf{q}\,\tilde{c}(q) + \mathbf{k}\cdot\mathbf{p}\,\tilde{c}(p))^2, \tag{36}$$

where $\mathbf{p} = \mathbf{k} - \mathbf{q}$. The equations of MCT, (34)–(36), capture slow structural relaxation, absent from the simple DDFT approximation (30), and predict dynamical arrest in dense and/or strongly attractive systems.[18] The MCT closure (35) is local in time but nonlocal in space. Relaxation of the restriction $\mathbf{m}(1,2) = 0$, generates an additional term within the time integral in (34), which is linear in the intermediate scattering function. Remarkably, this extension, which emerges naturally within the NOZ approach, is consistent with the "extended MCT" of Götze and Sjögren,[19] in which an additional relaxation process was introduced to describe relaxation processes ("hopping") in glassy states.

K. Connection to power functional theory

The NOZ approach developed in this work gains further significance when viewed in the context of the recently developed power functional theory,[9] which is an extension of classical density functional theory to nonequilibrium. Within this framework, minimization of a dynamic (free power) functional yields a general and exact equation of motion for the one-body current,

$$\mathbf{J}(1) = \mathbf{J}_{\mathrm{DDFT}}(1) - \frac{\rho(1)}{\gamma}\frac{\delta P^{\mathrm{exc}}_{t_1}[\rho,\mathbf{J}]}{\delta\mathbf{J}(1)}, \tag{37}$$

where $\mathbf{J}_{\mathrm{DDFT}}(1)$ is defined via (26) and obtained by differentiation of the ideal gas contribution to the power dissipation, $P^{\mathrm{id}}_t[\rho,\mathbf{J}] = \int d\mathbf{r}\gamma\mathbf{J}(\mathbf{r},t)^2/(2\rho(\mathbf{r},t))$, with respect to the one-body current. The excess (over ideal gas) power dissipation, $P^{\mathrm{exc}}_t[\rho,\mathbf{J}]$, is a functional of the history of $\rho(1)$ and $\mathbf{J}(1)$ prior to time t and accounts for dissipation induced by particle-particle interactions. Differentiating the exact Euler-Lagrange equation (37) with respect to $\beta\mathcal{V}(3)$ (following the same procedure used to obtain (27)) and comparing the result to the general form (33) yields the identification of the direct time correlation functions with second functional derivatives of the excess power dissipation via

$$\mathbf{m}(1,2) = -\gamma^{-1}\frac{\delta}{\delta\rho(2)}\frac{\delta P^{\mathrm{exc}}_{t_1}[\rho,\mathbf{J}]}{\delta\mathbf{J}(1)}, \tag{38}$$

$$\mathsf{M}(1,2)^{\mathsf{T}} = -\gamma^{-1}\frac{\delta}{\delta\mathbf{J}(2)}\frac{\delta P^{\mathrm{exc}}_{t_1}[\rho,\mathbf{J}]}{\delta\mathbf{J}(1)}, \tag{39}$$

where the superscript T indicates the transpose. Equations (33) and (37)–(39) imply that approximating a single mathematical object, the excess power dissipation functional, is sufficient to generate a closed and fully consistent set of equations for the dynamics of both the one- and two-body correlation functions. The DDFT approximation, leading to Eqs. (26) and (27), is obtained by setting $P^{\mathrm{exc}}_t[\rho,\mathbf{J}] = 0$.

A natural way to go beyond DDFT is to approximate $P^{\mathrm{exc}}_t[\rho,\mathbf{J}]$ by a truncated (functional) Taylor expansion in

the one-body current about the equilibrium state. To leading (quadratic) order this yields

$$P_t^{\rm exc}[\rho, \mathbf{J}] = -\frac{\gamma}{2}\int d\mathbf{r}_1 \int d2\ \mathbf{J}(1)\cdot \mathsf{M}(1,2)\Big|_{\mathbf{J}=0}\cdot \mathbf{J}(2). \quad (40)$$

Making the approximation $\mathsf{M}(1,2)|_{\mathbf{J}=0} \approx M_{\rm MCT}(1-2)\mathbf{1}$, which on the two-body level yields the MCT equation, generates on the one-body level a closed non-Markovian equation of motion for the current and density, via (7) and (37). This equation of motion contains information about slow structural relaxation, on the level of idealized MCT, and thus provides a useful tool to study situations for which standard DDFT fails, such as, e.g., the sedimentation of colloidal gels.[20]

III. CONCLUDING REMARKS

To summarize, we have developed a nonequilibrium Ornstein-Zernike approach to the two-time correlation functions of interacting Brownian particles. The most fundamental equations emerging from our treatment are (27) and (33) for the vectorial van Hove current. When supplemented by the two-body continuity equation (10), these expressions provide a means to calculate the two-time dynamical correlation functions under the influence of arbitrary external forces. Approximate closures, of which MCT is a specific nontrivial example, generate, in general, non-Markovian equations of motion for the van Hove function (8) and the van Hove current (9).

As part of our development of the general nonequilibrium theory we have derived a DDFT approximation for the van Hove current (27). This expression, which to the best of our knowledge has not appeared previously in the literature, provides much confidence in our general approach and strongly supports our identification of the microscopically defined two-time correlation functions, namely the van Hove function (8) and van Hove current (9), as functional derivatives of the one-body fields, via (20) and (21). The DDFT approximation to the van Hove current (27) predicts de Gennes narrowing of the intermediate scattering function for homogeneous systems and derives the inhomogeneous equilibrium OZ relation (2) in the equilibrium limit, consistent with the underlying adiabatic approximation.

One can view the general equations of motion (27) and (33) as the basis for the construction of approximate nonequilibrium integral equation theories. However, an alternative, and potentially more illuminating approach to a closed two-time theory is provided by the power functional formalism.[9] Within this framework, non-adiabatic contributions to the one-body equation of motion (37) and the memory functions entering the two-time equations (38) and (39), are related to first and second derivatives, respectively, of the excess power dissipation, as a single generating functional. In analogy with equilibrium DFT, for which the direct correlation function, $c(\mathbf{r}_1, \mathbf{r}_2)$, is generated from a free energy functional, the nonequilibrium time-direct correlation functions (memory functions) responsible for non-Markovian dynamics are generated by the excess power dissipation functional. As the same excess power dissipation functional generates the dynamics of the one-body fields, via the Euler-Lagrange equation (37), the power functional approach can be seen to provide a unified variational framework for the calculation of one- and two-body dynamical correlation functions. Further functional differentiation of (33) with respect to external forces generates higher-order NOZ relations involving, for example, three- and four-body correlations. Despite their complexity, these expressions may be of use, perhaps in a simplified form or in special limits, for analyzing dynamical heterogeneities in equilibrium or in metastable, arrested states.[21]

By expressing the MCT within the framework of functional differentiation, it is straightforward to identify a candidate approximation, (40), to the excess power dissipation functional, which can then be equally well applied, via (37), on the one-body level. This opens up the possibility of exploiting approximations developed on the two-body level (e.g., MCT) for one-body variational calculations, thus putting within reach the systematic investigation of many interesting problems for which the one-body dynamics may be significantly influenced by slow structural relaxation (e.g., the sedimentation of gels[20]). When applied to inhomogeneous driven systems the approximate excess dissipation functional (40), together with (10) and (33), provides a natural extension of equilibrium MCT. Moreover, application of (40) in a dynamic test particle calculation of the type developed by Archer *et al.*[12,13] may provide results for the intermediate scattering function which are superior to the standard MCT, as the calculation is performed at the one-body level. Research along all these lines is in progress.

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